

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
10 January 2002 (10.01.2002)

PCT

(10) International Publication Number
WO 02/02698 A1

- (51) International Patent Classification⁷: C09D 5/16
- (21) International Application Number: PCT/EP01/07227
- (22) International Filing Date: 26 June 2001 (26.06.2001)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
00305726.2 6 July 2000 (06.07.2000) EP
- (71) Applicant: **INTERNATIONAL COATINGS LIMITED**
[GB/GB]; Oriel House, 16 Connaught Place, London W2
2ZB (GB).
- (72) Inventors: **LINES, Robert**; 14 Parklands, Northumberland, Ponteland NE20 9LL (GB). **FINNIE, Alistair, Andrew**; 11 Felton Avenue, Whitley Bay, Tyne & Wear NE25 8TQ (GB). **FOX, John**; 14 Burlington Court, Hadrian Park Estate, Wallsend, Tyne & Wear NE28 9YH (GB).
- (74) Agent: **SCHALKWIJK, Pieter, Cornelis**; Akzo Nobel N.V., Intellectual Property Dept. (Dept. AIP), P.O. Box 9300, NL-800 SB Arnhem (NL).
- (81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW.
- (84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).
- Published:**
— with international search report
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 02/02698 A1

(54) Title: ANTIFOULING PAINT

(57) Abstract: The invention relates to an antifouling paint having a binder comprising a rosin material and an auxiliary film-forming resin, the paint including an ingredient having marine biocide properties, wherein the binder comprises a blend of the rosin material and an auxiliary film-forming resin in ratio 20:80 to 95:5 % by weight, the auxiliary film-forming resin comprising 20-100 % by weight of an acid-functional film forming polymer (A) whose acid groups are blocked by groups capable of hydrolyzing, dissociating or exchanging with seawater species to leave a polymer soluble in seawater, the blocking groups being selected from quaternary ammonium groups which form a quaternary ammonium salt of the polymer and quaternary phosphonium groups which form a quaternary phosphonium salt of the polymer, and 80-20 % of a non-hydrolyzing water-insoluble film-forming polymer (B).

ANTIFOULING PAINT

- 5 This invention relates to antifouling paint. An antifouling paint is used as a top coat on ships' hulls to inhibit the settlement and growth of marine organisms such as barnacles and algae, generally by release of a biocide for the marine organisms.
- 10 Traditionally, antifouling paints have comprised a relatively inert binder with a biocidal pigment which is leached from the paint. Among the binders which have been used are vinyl resins and rosin. The vinyl resins are seawater-insoluble and paints based on them use a high pigment concentration so that there is contact between pigment particles to ensure
- 15 leaching. Rosin is a hard brittle resin which is very slightly soluble in seawater. Rosin-based antifouling paints have been referred to as soluble matrix or eroding paints. The biocidal pigment is very gradually leached out of the matrix of rosin binder in use, leaving a skeletal matrix of rosin which becomes washed off the hull surface to allow leaching of the biocidal
- 20 pigment from deep within the paint film.

Many successful antifouling paints in recent years have been "self-polishing copolymer" paints based on a polymeric binder to which biocidal tri-organotin moieties are chemically bound and from which the biocidal

25 moieties are gradually hydrolyzed by seawater, as described for example in GB-A-1457590. Self-polishing copolymer paints which release non-biocidal moieties are described in EP-A-69559, EP-A-204456, EP-A-529693, EP-A-779304, WO-A-91/14743, WO-A-91/09915, GB-A-231070 and JP-A-9-286933.

30

US-A-4675051 describes a marine antifouling paint which is gradually dissolved in seawater and which comprises a binder which is a resin

CONFIRMATION COPY

produced by the reaction of rosin and an aliphatic polyamine containing at least one primary or secondary amine group. EP-A-802243 describes a coating composition comprising a rosin compound, a polymer containing organosilyl ester groups and an antifoulant.

5

Rosin is not a very good film-former, and it is known to add other film-forming resins to rosin based antifouling paints. This has sometimes led to paints which were difficult to wash off the hull surface. The present invention seeks to improve rosin-based antifouling paints with respect to the strength of the paint film and/or the reliable eroding away of the rosin-based paint matrix after biocide has been leached from the paint.

An antifouling paint according to the present invention has a binder comprising a rosin material and an auxiliary film-forming resin, the paint including an ingredient having marine biocide properties, characterized in that the binder comprises a blend of the rosin material and an auxiliary film-forming resin in ratio 20:80 to 95:5% by weight, the auxiliary film-forming resin comprising 20-100% by weight of an acid-functional film forming polymer (A) whose acid groups are blocked by groups capable of hydrolyzing, dissociating or exchanging with seawater species to leave a polymer soluble in seawater, the blocking groups being selected from quaternary ammonium groups which form a quaternary ammonium salt of the polymer and quaternary phosphonium groups which form a quaternary phosphonium salt of the polymer, and 80-20% of a non-hydrolyzing water-insoluble film-forming polymer (B).

The rosin material is preferably rosin, particularly wood rosin or alternatively tall rosin or gum rosin. The main chemical constituent of rosin is abietic acid. The rosin can be any of the grades sold commercially, preferably that sold as WW (water white) rosin. The rosin material can alternatively be a rosin derivative, for example a maleinised or fumarised rosin, hydrogenated

rosin, formylated rosin or polymerised rosin, or a rosin metal salt such as calcium, magnesium, copper or zinc rosinate.

- The acid-functional film forming polymer (A) whose acid groups are blocked
5 by groups capable of hydrolyzing, dissociating or exchanging with seawater species to leave a polymer soluble in seawater is preferably an acid-functional polymer whose acid groups are blocked by quaternary ammonium groups which form a quaternary ammonium salt of the polymer. The quaternary ammonium group can be tetra-alkyl or it can contain one or
10 more alkoxyalkyl, cycloalkyl, aryl or aralkyl groups. More generally the organic groups in the quaternary ammonium group may be saturated or unsaturated, aliphatic, cycloaliphatic, aromatic, aliphatic-aromatic or heterocyclic.
- 15 The quaternary ammonium moiety preferably contains at least one organic group containing at least 3 carbon atoms, advantageously at least 8 carbon atoms and preferably from 8 to 25 carbon atoms (for example 8 to 20 carbon atoms), and more especially from 12 to 25 carbon atoms. The polymers containing a relatively long chain quaternary ammonium group
20 have a decreased rate of dissolution in seawater. Examples of such quaternary ammonium groups are dodecyl trimethyl ammonium, hexadecyl trimethyl ammonium, octadecyl trimethyl ammonium, oleyl trimethyl ammonium, benzyl dodecyl dimethyl ammonium, dodecyl dimethyl octyl ammonium or trioctyl methyl ammonium. Mixtures of quaternary ammonium
25 groups can be used; for example an organic group having 8 to 20 carbon atoms can be derived from a naturally occurring material such as a natural fatty material. Examples of such mixed quaternary ammonium groups are trimethyl hydrogenated tallow ammonium, dimethyl di(hydrogenated tallow) ammonium or trimethyl coconut ammonium. The quaternary group can
30 alternatively be derived from rosin, for example it can be the N,N,N-trimethyl derivative of the amine sold commercially as "Rosin Amine D",

being mainly dehydroabietyl trimethyl ammonium. Advantageously, the total number of carbon atoms in the quaternary ammonium moiety is 8 or more, preferably 12 or more (for example, from 12 to 40).

- 5 The acid-functional film forming polymer (A) whose acid groups are blocked by groups capable of hydrolyzing, dissociating or exchanging with seawater species to leave a polymer soluble in seawater is alternatively an acid-functional polymer whose acid groups are blocked by quaternary phosphonium groups which form a quaternary phosphonium salt of the
10 polymer. The quaternary phosphonium group can be tetra-alkyl or it can contain one or more alkoxyalkyl, cycloalkyl, aryl or aralkyl groups. More generally the organic groups in the quaternary phosphonium group may be saturated or unsaturated, aliphatic, cycloaliphatic, aromatic, aliphatic-aromatic or heterocyclic. Examples of such quaternary phosphonium
15 groups are tetrabutylphosphonium, tetraphenylphosphonium and stearyltributylphosphonium.

The acid-functional polymer is preferably an addition copolymer of an olefinically unsaturated carboxylic acid, sulphonic acid, acid sulphate ester,
20 phosphonic acid or acid phosphate ester and at least one unsaturated comonomer. The unsaturated carboxylic acid can for example be acrylic or methacrylic acid or an acid functional ester or amide of acrylic acid or methacrylic acid such as mono-2-(methacryloyloxy)ethyl succinate, mono-2-(methacryloyloxy)ethyl phthalate, 2-acrylamidoglycolic acid, or 3-
25 acrylamido-3-methylbutyric acid. The unsaturated sulphonic acid can for example be 2-acrylamido-2-methylsulphonic acid (AMPS). The unsaturated comonomer can for example be an ester or amide of an alkyl, alkoxyalkyl, carbocyclic or heterocyclic alcohol or amine with an unsaturated carboxylic acid, such as methyl acrylate or methacrylate, butyl acrylate or
30 methacrylate and isobornyl acrylate or methacrylate and the like.

Alternatively the unsaturated co-monomer may be a vinylic compound, for example styrene, vinyl pyrrolidone or vinyl acetate.

The acid-functional film forming polymer (A) whose acid groups are blocked
5 by quaternary ammonium groups which form a quaternary ammonium salt
of the polymer can be prepared by reaction of a polymer containing acid or
acid-salt groups with a quaternary ammonium compound. Alternatively, it
can be prepared by polymerisation of a quaternary ammonium salt of an
ethylenically unsaturated acid-functional monomer formed, for example, by
10 reaction of an ethylenically unsaturated monomer containing acid or acid-
salt groups with a quaternary ammonium compound. Examples of suitable
acid-salts groups include metal salts such as sodium, potassium and lithium
salts, or amine salts such as ammonium or hydroxyethyldimethylammonium
salts and the like. Examples of suitable quaternary ammonium compounds
15 include quaternary ammonium hydroxides, carbonates, bicarbonates,
sulphates, bisulphates or halides.

The acid-functional film forming polymer (A) whose acid groups are blocked
by quaternary phosphonium groups which form a quaternary phosphonium
20 salt of the polymer can be prepared by similar methods to those used to
prepare the acid-functional film forming polymer (A) whose acid groups are
blocked by quaternary ammonium groups, using a quaternary phosphonium
compound in place of the quaternary ammonium compound.

25 As a further possibility, when the acid-functional film forming polymer (A)
whose acid groups are blocked by quaternary ammonium or quaternary
phosphonium groups is a copolymer of an olefinically unsaturated sulphonic
acid, the quaternary ammonium or quaternary phosphonium group may be
introduced by reaction of a sulphonate ester, for example a
30 methylsulphonate ester, with a tertiary amine or tertiary phosphine. The
sulphonate ester may be in monomeric or polymeric form. If the ester is in

monomeric form, the resulting quaternary ammonium or quaternary phosphonium salt of an olefinically unsaturated sulphonic acid-functional monomer is then polymerised for use according to the present invention.

5 The non-hydrolyzing water-insoluble film-forming polymer (B) can for example be a vinyl ether polymer, for example a poly(vinyl alkyl ether) or a copolymer of a vinyl alkyl ether with vinyl acetate or vinyl chloride, an acrylate ester polymer such as a homopolymer or copolymer of one or more alkyl acrylates or methacrylates which preferably contain 1 to 6
10 carbon atoms in the alkyl group and may contain a co-monomer such as acrylonitrile or styrene, or a vinyl acetate polymer such as polyvinyl acetate or a vinyl acetate vinyl chloride copolymer. The polymer (B) can alternatively be a polyamine, particularly a polyamide having a plasticising effect such as a polyamide of a fatty acid dimer or the polyamide sold under
15 the Trademark "Santiciser".

We have found that the paints of the invention have the optimum combination of film-forming and eroding properties when the non-hydrolyzing water-insoluble film-forming polymer (B) is present in the
20 composition, albeit as a minor proportion of the auxiliary film-forming resin. Most preferably the weight ratio of rosin to total auxiliary film-forming resin is from 25:75, 50:50 or 55:45 up to 80:20. The hydrolyzing or dissociating film-forming polymer (A) preferably forms at least 30, most preferably at least 50, up to 80 or 90% by weight of the auxiliary film-forming resin, the
25 non-hydrolyzing water-insoluble polymer (B) being the remainder.

The antifouling paint can include a non-polymeric plasticiser. Such a plasticiser can for example be present at up to 50% by weight based on the total binder polymer, most preferably at least 10% and up to 35% by weight
30 based on binder polymer. Examples of such plasticisers are phthalate esters such as dibutyl phthalate, butyl benzyl phthalate or dioctyl phthalate,

phosphate triesters such as tricresyl or tris(isopropyl)phenyl phosphate, or chlorinated paraffins.

The rosin and the polymers forming the auxiliary film-forming resin can be
5 mixed in a common solvent which forms at least part of the paint solvent,
for example an aromatic hydrocarbon such as xylene, toluene or
trimethylbenzene, an alcohol such as n-butanol, an ether alcohol such as
butoxyethanol or methoxypropanol, an ester such as butyl acetate or
isoamyl acetate, an ether-ester such as ethoxyethyl acetate or
10 methoxypropyl acetate, a ketone such as methyl isobutyl ketone or methyl
isoamyl ketone, an aliphatic hydrocarbon such as white spirit, or a mixture
of two or more of these solvents. The paint can alternatively be water-
based, for example it can be based on a commercial aqueous rosin
dispersion.

15

The ingredient having marine biocidal properties usually is a biocide for
aquatic organisms or a pigment. This biocide or pigment can be mixed with
the binder using conventional paint-blending techniques. The biocide may
itself be all or part of the pigment of the paint. The coating composition
20 preferably has a pigment volume concentration of, for example, 15 to 55%.
The pigment preferably comprises at least one sparingly soluble
metalliferous pigment having a solubility in seawater of from 0.5 to 10 parts
per million by weight. Examples of such pigments which are also aquatic
biocides include copper or zinc compounds, such as cuprous oxide,
25 cuprous thiocyanate, cuprous sulphate, zinc ethylene bis(dithiocarbamate),
zinc dimethyl dithiocarbamate, zinc pyrrhione, copper pyrrhione, zinc
diethyl dithiocarbamate, copper resinate or cuprous ethylene
bis(dithiocarbamate). Other sparingly soluble pigments having a solubility in
sea water of 0.5 to 10 parts per million include barium sulphate, calcium
30 sulphate, dolomite and zinc oxide. Mixtures of sparingly soluble pigments
can be used, for example cuprous oxide, cuprous thiocyanate or zinc

ethylene bis(dithiocarbamate), which are highly effective biocidal pigments, can be mixed with zinc oxide, which is not effective as a biocide but dissolves slightly more rapidly in seawater. Copper metal can be present as an aquatic biocide, for example in flake or powder form.

5

The antifouling coating composition can contain a non-metalliferous biocide for marine organisms, for example tetramethyl thiuram disulphide, methylene bis(thiocyanate), captan, pyridiniumtriphenylboron, a substituted isothiazolone such as 4,5-dichloro-2-n-octyl-4-isothiazolin-3-one, 2-
10 methylthio-4-t.butylamino-6-cyclopropylamino-s-triazine, N-3,4 dichlorophenyl-N',N'-dimethyl-urea ("Diuron"), 2-(thio-cyanomethylthio) benzothiazole, 2,4,5,6-tetrachloro-isophthalonitrile, dichlorofluanid, tolylfluorid or 2,3,5,6-tetrachloro-4-(methyl-sulphonyl)pyridine. Such a non-metalliferous biocide can be used as the only biocide of the coating in a
15 copper-free, or even metal-free or pigment-free, antifouling coating. Many of these non-metalliferous biocides are solid and all are sparingly soluble in seawater and may help the "self-polishing" action of the paint.

The coating composition can additionally contain a pigment which is not
20 reactive with seawater and may be highly insoluble in seawater (solubility below 0.5 part per million by weight) such as titanium dioxide or ferric oxide or an organic pigment such as phthalocyanine or azo pigment. Such highly insoluble pigments are preferably used at less than 60% by weight of the total pigment component of the paint, most preferably less than 40%. The
25 coating composition can additionally contain conventional thickeners, particularly thixotropes such as silica or bentonite and/or stabilisers, for example zeolites or aliphatic or aromatic amines such as dehydroabietylamine.

The invention will be elucidated with reference to the following examples. These are intended to illustrate the invention but are not to be construed as limiting in any manner the scope thereof.

5

Examples

The following materials were mixed in the stated % by weight in a high speed disperser to form antifouling paints according to the invention.

10

| Compound | Example No.: | |
|---|--------------|-------|
| | 1 | 2 |
| Rosin | 9.96 | 9.96 |
| Hydrolysable acrylic Polymer (A1) | 5.49 | - |
| Hydrolysable acrylic Polymer (A2) | - | 5.49 |
| Non-hydrolyzing acrylic polymer (B1) | 2.62 | 2.62 |
| Tris(isopropylphenyl) phosphate plasticiser | 5.09 | 5.09 |
| Red copper oxide | 37.48 | 37.48 |
| Zinc Oxide | 11.85 | 11.85 |
| Zinc ethylene bis(dithiocarbamate) | 2.05 | 2.05 |
| Copper pyrithione | 1.98 | 1.98 |
| Natural iron oxide | 3.16 | 3.16 |
| Solvent | 17.64 | 17.64 |
| Additives | 2.68 | 2.68 |

Acrylic polymer A1 is a copolymer of the trimethyl (hydrogenated tallow)ammonium salt of mono-2-(methacryloyloxy) ethylsuccinate, styrene and isobornyl methacrylate in the mole ratio 25.0:30.0:45.0.

15

Acrylic polymer A2 is a copolymer of the hexadecyltrimethylammonium salt of 2-acrylamido-2-methylpropanesulphonic acid, isobornyl methacrylate and isobornyl acrylate in mole ratio 27.5:47.5:25.

- 5 Acrylic polymer B1 is a n-butyl acrylate polymer sold under the Trademark "Acronal 4F".

The solvent comprised mainly xylene with minor amounts of methyl isoamyl ketone, methyl isobutyl ketone and n-butanol. The rosin and acrylic polymers
10 were dissolved in solvent before being mixed with the other paint ingredients.

Additives comprised an organo-clay structuring agent, silica, carbon black and molecular sieve zeolite.

- 15 As a test of antifouling performance the paints of Examples 1 and 2 were each applied to plywood boards which had been pre-painted with a commercial anti-corrosive primer and the boards were immersed in the sea at Newton Ferrers, Devon, England. As a comparative test, primed boards were coated with a rosin paint having a formulation similar to Example 1 but containing extra
20 "Acronal 4F" in place of the hydrolysable acrylic polymer. The paint films were periodically assessed for settlement of marine fouling organisms and the results are shown below.

In all results quoted below, 100 = Totally clean, 0 = Totally fouled.

25

| Example | Average fouling rating |
|-------------|------------------------|
| 1 | 83 |
| 2 | 88 |
| Comparative | 60 |

Claims

1. An antifouling paint having a binder comprising a rosin material and an auxiliary film-forming resin, the paint including an ingredient having marine biocide properties, characterised in that the binder comprises a blend of the rosin material and an auxiliary film-forming resin in ratio 20:80 to 95:5% by weight, the auxiliary film-forming resin comprising 20-100% by weight of an acid-functional film forming polymer (A) whose acid groups are blocked by groups capable of hydrolyzing, dissociating or exchanging with seawater species to leave a polymer soluble in seawater, the blocking groups being selected from quaternary ammonium groups which form a quaternary ammonium salt of the polymer and quaternary phosphonium groups which form a quaternary phosphonium salt of the polymer, and 80-20% of a non-hydrolyzing water-insoluble film-forming polymer (B).
2. An antifouling paint according to claim 1 characterised in that the rosin material is rosin.
3. An antifouling paint according to claim 1 or claim 2, characterised in that the binder comprises a blend of the rosin material and the auxiliary film-forming resin in a ratio of 55:45 to 80:20 by weight.
4. An antifouling paint according to any one of claims 1 to 3, characterised in that the auxiliary film-forming resin comprises 30-90% by weight of the film-forming polymer (A) capable of hydrolyzing or dissociating to a polymer soluble in sea water and 70-10% by weight of the non-hydrolyzing water-insoluble film-forming polymer (B).
5. An antifouling paint according to any one of claims 1 to 4, characterised in that the film-forming polymer (A) is a quaternary ammonium salt of an

addition copolymer of an olefinically unsaturated sulphonic acid or acid sulphate ester and at least one olefinically unsaturated co-monomer.

6. An antifouling paint according to any one of claims 1 to 4, characterised in
5 that the film-forming polymer (A) is a quaternary ammonium salt of an addition copolymer of an olefinically unsaturated carboxylic acid and at least one olefinically unsaturated co-monomer.
7. An antifouling paint according to claim 5 or claim 6, characterised in that
10 the quaternary ammonium group contains at least one aliphatic hydrocarbon group having 8 to 25 carbon atoms.
8. An antifouling paint according to any one of claims 1 to 7, characterised in
15 that the non-hydrolyzing water-insoluble film-forming polymer (B) is an acrylate ester polymer or a vinyl ether polymer.
9. An antifouling paint according to any of one claims 1 to 8, characterised in that the binder includes a non-polymeric plasticiser present at up to 50% by weight based on the total binder polymer.

INTERNATIONAL SEARCH REPORT

Int. Application No
PCT/EP 01/07227

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C09D5/16

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

PAJ, EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|------------|---|-----------------------|
| A | PATENT ABSTRACTS OF JAPAN vol. 013, no. 384 (C-629), 24 August 1989 (1989-08-24) & JP 01 131286 A (DAINIPPON INK & CHEM INC;OTHERS: 01), 24 May 1989 (1989-05-24) abstract | 1 |
| A | PATENT ABSTRACTS OF JAPAN vol. 009, no. 145 (C-287), 20 June 1985 (1985-06-20) & JP 60 028456 A (NIPPON YUSHI KK), 13 February 1985 (1985-02-13) abstract | 1 |
| A | US 4 221 839 A (M&T CHEMICALS INC.) 9 September 1980 (1980-09-09) claims | 1 |
| -/-- | | |

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *G* document member of the same patent family

Date of the actual completion of the international search

2 October 2001

Date of mailing of the international search report

17/10/2001

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Girard, Y

INTERNATIONAL SEARCH REPORT

In International Application No
PCT/EP 01/07227

| C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT | | |
|--|--|-----------------------|
| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
| A | <p>US 5 302 192 A (COURTAULDS COATINGS) 12 April 1994 (1994-04-12) abstract</p> <p>-----</p> | 1 |

INTERNATIONAL SEARCH REPORT

Int. Application No.

PCT/JP 01/07227

| Patent document cited in search report | | Publication date | Patent family member(s) | Publication date |
|---|---|---------------------|----------------------------|---------------------|
| JP 01131286 | A | 24-05-1989 | JP 2614467 B2 | 28-05-1997 |
| JP 60028456 | A | 13-02-1985 | NONE | |
| US 4221839 | A | 09-09-1980 | NL 7703305 A | 02-10-1978 |
| | | | AU 523839 B2 | 19-08-1982 |
| | | | AU 3446978 A | 27-09-1979 |
| | | | BE 865294 A2 | 17-07-1978 |
| | | | CA 1111981 A1 | 03-11-1981 |
| | | | DE 2812602 A1 | 05-10-1978 |
| | | | DK 128578 A | 29-09-1978 |
| | | | FR 2385779 A1 | 27-10-1978 |
| | | | GB 1584943 A | 18-02-1981 |
| | | | IT 1218833 B | 24-04-1990 |
| | | | JP 53127534 A | 07-11-1978 |
| | | | NO 780987 A ,B, | 29-09-1978 |
| | | | PT 67767 A | 01-04-1978 |
| US 5302192 | A | 12-04-1994 | AT 141317 T | 15-08-1996 |
| | | | BR 9007943 A | 06-10-1992 |
| | | | DE 69028116 D1 | 19-09-1996 |
| | | | DE 69028116 T2 | 13-02-1997 |
| | | | DK 506782 T3 | 14-10-1996 |
| | | | EP 0506782 A1 | 07-10-1992 |
| | | | ES 2091909 T3 | 16-11-1996 |
| | | | WO 9109915 A1 | 11-07-1991 |
| | | | GR 3021554 T3 | 28-02-1997 |
| | | | JP 2994749 B2 | 27-12-1999 |
| | | | JP 5504365 T | 08-07-1993 |
| | | | NO 303583 B1 | 03-08-1998 |
| | | | PT 96346 A ,B | 15-10-1991 |
| | | | SG 45228 A1 | 16-01-1998 |

(18)



Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number:

**0 069 559
B1**

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication of patent specification: 02.05.85

(51) Int. Cl.⁴: C 09 D 5/16

(71) Application number: 82303486.3

(22) Date of filing: 02.07.82

(54) Marine paint.

(30) Priority: 03.07.81 GB 8120569

(43) Date of publication of application:
12.01.83 Bulletin 83/02

(45) Publication of the grant of the patent:
02.05.85 Bulletin 85/18

(84) Designated Contracting States:
DE FR IT NL SE

(58) References cited:
FR-A-2 266 733

CHEMICAL ABSTRACTS, vol. 92, 1980, page 35,
no. 199253n, Columbus, Ohio, USA

(73) Proprietor: INTERNATIONAL PAINT Public
Limited Company
Henrietta House 9 Henrietta Place
London W1A 1AD (GB)

(72) Inventor: Sghibartz, Cristian Marius
18, Sunningdale Drive
Washington Tyne and Wear NE37 2LL (GB)

(74) Representative: Newby, John Ross et al
J.Y. & G.W. Johnson Furnival House 14/18 High
Holborn
London WC1V 6DE (GB)

EP 0 069 559 B1

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European patent convention).

Courier Press, Leamington Spa, England.

Description

This invention relates to marine anti-fouling paints generally used as top-coat paints for ships' hulls.

The growth of marine organisms on the sub-marine parts of a ship's hull increases the frictional resistance of the hull to passage through water, leading to increased fuel consumption and/or a reduction in the speed of the ship. Marine growths accumulate so rapidly that the remedy of cleaning and repainting as required is impractical. In general, the extent of fouling is limited by applying to the hull a top-coat incorporating anti-fouling agents. The anti-fouling agents are biocides which are freed from the surface of the paint over a period in concentrations lethal to marine organisms on the hull's surface. The anti-fouling paint fails only when the concentration of biocide available at the paint surface falls below the lethal concentrations, and with marine paints up to two years of useful life can be expected. The better anti-fouling paints are thus effective in dealing with gross infestation of hulls for considerable periods but a top-coat paint of a ship's sub-marine surface has irregularities from its method of application and is furthermore subject to breakdown and delamination during service, increasing the roughness of the hull so that the performance of the ship falls off even when fouling is prevented.

According to the present invention, a marine paint comprises a film-forming copolymer which is a copolymer containing 20 to 80 per cent by weight of units of a quinolinyl or substituted quinolinyl ester of an olefinically unsaturated carboxylic acid, the balance of the copolymer being units of at least one olefinically unsaturated comonomer, and a metalliferous pigment which is sparingly soluble in sea-water.

The paint of the present invention has the remarkable property that relatively moving sea-water smooths the surface of the paint, removing excrescences composed of the paint. When it is painted on a ship, the painted sub-marine surface of the ship at least preserves its initial smoothness and may become smoother during the ordinary traffic of the ship, leading to improved efficiency. Our British patent specification 1,457,590 describes and claims a paint having this remarkable property and Figures 2A—2D in particular of the drawings accompanying British patent specification 1,457,590 illustrate the smoothing effect of the relatively moving sea-water. A similar smoothing effect is achieved with the paint of the present invention. The paint described and claimed in British patent specification 1,457,590 is based on a film-forming copolymer containing units of a triorgano tin salt of an olefinically unsaturated carboxylic acid. Upon contact with sea-water it loses triorgano tin ions by ion exchange with sea-water. This generates a water-soluble resin which essentially is a copolymer salt formed as a result of the depletion in the copolymer organotin content and

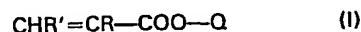
exchange with metal ions present in sea-water. The smoothing of paint described in British patent specification 1,457,590 is thus inevitably accompanied by the release of organotin ions into the surrounding sea-water. In most circumstances this is useful, because the triorgano tin ions are effective anti-fouling agents. However, triorgano tin ions are expensive to employ and are strongly biocidal and there are some circumstances where the release of triorgano tin ions is preferably avoided or reduced whilst still obtaining the benefits of smoothing of the paint in service. The present invention provides a self-smoothing paint which does not release such strongly biocidal ions.

The paint of the present invention generates a water-soluble residue by exchange of quinolinyl (or substituted quinolinyl) groups in the polymer for metal ions present in the sea-water. The quinolinyl groups are released into the sea-water. These are generally not toxic to animal life, although they have some effect in inhibiting fouling by algae and seaweed. Generally, the metalliferous pigment is chosen to have biocidal activity or a separate anti-fouling agent is used in paints according to the invention. This can be chosen for the particular waters which a ship is likely to encounter.

If desired, the film-forming copolymer can also contain units of a triorgano tin salt of an olefinically unsaturated carboxylic acid and these units can replace a part of the units of the quinolinyl (or substituted quinolinyl) ester.

The invention therefore also provides a marine paint which comprises a film-forming copolymer and a metalliferous pigment which is sparingly soluble in sea-water, and in which the copolymer comprises 10—80 per cent by weight of (a) units of a quinolinyl or substituted quinolinyl ester of an olefinically unsaturated carboxylic acid, up to 60 per cent by weight of (b) units of a triorgano tin salt of an olefinically unsaturated carboxylic acid, (a) and (b) together forming 20—80 per cent by weight of the copolymer, and the balance of the copolymer being (c) units of at least one olefinically unsaturated comonomer.

The quinolinyl or substituted quinolinyl ester of an olefinically unsaturated carboxylic acid preferably has the formula



where R is a hydrogen atom or methyl group, R' is hydrogen or —COOQ and Q is a 8-quinolinyl group optionally substituted by one or more alkyl or alkoxy groups having 1 to 4 carbon atoms, halogen atoms, nitro, cyano or substituted acid amide groups. Compounds of formula (I) can be made by reaction of the corresponding 8-hydroxy quinoline with acrylyl or methacrylyl chloride. The ester (I) is preferably unsubstituted quinolinyl acrylate or methacrylate; halogenated derivatives such as 7-bromo-5-chloro-quinolinyl-8 acrylate are an alternative.

The olefinically unsaturated comonomer can be

an acrylic monomer, for example methyl methacrylate, methyl acrylate, ethyl acrylate, propyl acrylate, butyl acrylate, amyl acrylate, hexyl acrylate, the corresponding esters of methacrylic acid, acrylonitrile or methacrylonitrile, or a vinyl monomer, for example vinyl acetate, vinyl butyrate, vinyl chloride, styrene or vinyl pyridine. The polymer can also contain monomer units conferring increased water-reactivity, particularly when the polymer contains a relatively low proportion of monomer units (a) or monomer units (a) and (b). For example, the polymer can contain up to 20 per cent by weight of maleic or itaconic anhydride, acrylamide, methacrylamide or N-vinyl pyrrolidone units or up to 5 per cent by weight, preferably 2 per cent or less, of acrylic, methacrylic or itaconic acid units. Care must be taken to avoid gelation of the paint when using a copolymer containing free acid monomer units.

The monomer units (b) are preferably of the formula $R_3SnOOCCH=CHR'$ where each R is an alkyl radical containing 2 to 8 carbon atoms or an aryl or aralkyl radical, R' is H or CH_3 and R'' is H or $-COOSnR_3$. The groups R attached to the tin atom can be different but are preferably the same, for example R_3Sn can be tributyl tin, tripropyl tin, tribenzyl tin, triphenyl tin, tritolyl tin or trihexyl tin. The carboxylate group $-OOCCH=CHR'$ is preferably acrylate, methacrylate or maleate.

If triorgano tin salt units are not present the film-forming copolymer preferably comprises 20—60 per cent by weight of the quinolinyl (or substituted quinolinyl) ester units and 40—80 per cent by weight of units of the comonomer, for example at least one alkyl acrylate or methacrylate. If triorgano tin salt units are present the copolymer preferably comprises 15—40 per cent by weight of the quinolinyl (or substituted quinolinyl) ester units (a), 20—45 per cent by weight of the triorgano tin salt units (b), for example tributyl tin methacrylate units, and 30—50 per cent by weight of units of at least one alkyl acrylate or methacrylate.

The film-forming copolymers can be prepared by free radical polymerisation under polymerisation conditions, generally using a catalyst such as benzoyl peroxide or azobisisobutyronitrile in an organic solvent such as xylene, toluene, butyl acetate, 2-ethoxyethanol, 2-methoxyethanol, 2-ethoxyethyl acetate, methyl isobutyl ketone, butanol and/or cyclohexanone or in aqueous emulsion. For solvent polymerisation mixtures of xylene with minor amounts, for example up to 20 per cent by volume, of 2-ethoxyethanol, 2-ethoxyethyl acetate or methyl isobutyl ketone may be preferred. Polymerisation is preferably carried out at a temperature in the range 70—100°C.

The metalliferous pigment sparingly soluble in sea-water may alternatively be described as a substantially water-insoluble metalliferous pigment capable of reacting with sea-water. It is exemplified by cuprous thiocyanate, cuprous oxide zinc oxide, zinc chromate, cupric acetate metaarsenate, and zinc ethylene bis(dithio-

carbamate). These pigments produce water-soluble metal compounds on reaction with sea-water so that the pigment particles do not survive at the paint surface. Preferably, the sparingly soluble pigment has a solubility in sea-water of from about 1 to about 10 parts per million by weight. The pigment has the effect of inducing the overall smoothing which the relatively moving sea-water exerts on the paint film, minimising localised erosion and preferentially removing excrescences formed during application of the paint. Mixtures of such pigments can be used, for example zinc oxide, which is most effective at inducing the gradual dissolution of the paint, can be mixed with cuprous oxide, cuprous thiocyanate or zinc ethylene bis(dithiocarbamate), which are more effective marine biocides. The ratio of zinc oxide to cuprous oxide or thiocyanate can for example be 1:1 to 9:1 by weight.

The paint composition can additionally contain a pigment which is highly insoluble in sea-water (solubility below 1 ppm by weight), such as titanium dioxide or ferric oxide. Such highly insoluble pigments can be used in proportions up to 40 per cent by weight of the total pigment component of the paint, but preferably are used in proportions of less than 20 per cent by weight. The highly insoluble pigment has the effect of retarding the dissolution of the paint.

The proportion of pigment to copolymer is preferably such as to give a pigment volume concentration which is above 25 per cent in the dry paint film but below the critical pigment volume concentration; most preferably the pigment volume concentration is 35—50 per cent.

Polymers containing the quinolinyl (or substituted quinolinyl) ester may be somewhat brittle, particularly those containing a high proportion of a quinolinyl methacrylate. The paints according to the invention may therefore include a plasticiser, for example tritolyl phosphate, diisooctyl phthalate, tributyl phosphate, butyl benzyl phthalate, 'Lutonal A25' polyether or dibutyl tartrate. Alternatively, the olefinically unsaturated comonomer can be chosen to reduce the brittleness of the copolymer. Examples of comonomers which reduce brittleness are alkyl acrylates containing three or more carbon atoms in the alkyl group, for example butyl acrylate, hexyl acrylate or 2-ethylhexyl acrylate.

If the rate of dissolution in relatively moving sea-water of a combination of the polymer containing quinolinyl (or substituted quinolinyl) ester units and a pigment sparingly soluble in sea-water is undesirably rapid, for example when the polymer contains a relatively high proportion of quinolinyl (or substituted quinolinyl) ester and triorgano tin salt units, the rate of dissolution can be retarded by including in the paint a hydrophobic organic compound which retards the dissolution of the paint. Examples of such hydrophobic organic retarders are methyl phenyl silicon fluids, for example silicone fluid DC550 sold by Dow Corning Ltd., chlorinated diphenyl, for example Aroclor 1254 sold by Monsanto Ltd,

chlorinated paraffin wax, for example Cereclor 48 and Cereclor 70 sold by I.C.I. Ltd., diphenyl ether, dichlorodiphenyltrichloroethane and low molecular weight polybutenes, for example Hyvis 05 sold by B.P. Ltd. The hydrophobic organic retarder, for example chlorinated diphenyl or chlorinated paraffin wax, may also be a plasticiser for the paint.

Many of the sparingly sea-water soluble metal-liferous pigments have some biocidal activity, particularly zinc ethylene bis(dithiocarbamate) and copper compounds such as cuprous thiocyanate, cupric acetate metaarsenate and cuprous oxide but also zinc oxide to a lesser extent. Even when the copolymer contains no triorgano tin salt units (b), the biocidal effect of the sparingly sea-water soluble pigments, particularly zinc ethylene bis(dithiocarbamate) and cuprous oxide, may be sufficient so that the paint needs no further biocide, for example in the case of paint for use on the flat bottom of very large tankers, where fouling is less likely to occur. We believe that the self-smoothing action of the paint increases its resistance to fouling compared to a conventional paint releasing biocide at the same rate. This effect is more marked with increasing rate of dissolution of the paint.

The paint can contain an added biocide effective against seaweed and barnacles. Triorgano tin salts and oxides such as triphenyltin fluoride, tributyl tin fluoride, tributyl tin dibromosuccinate, triphenyltin chloride, triphenyltin hydroxide and tributyltin oxide are effective marine biocides and can be used in paints according to the invention, particularly where the polymer contains no monomer units (b). A paint according to the invention comprising a tin-free polymer, a pigment such as cuprous oxide and a small proportion of a triorgano tin salt (up to 25 per cent by volume based on the pigment) may have antifouling and smoothing properties equal to an organo tin copolymer paint of much higher total organo tin content. Alternatively a mixture of organo tin-free and organo tin-containing polymers can be used.

In some cases it will be desired to avoid completely the release of triorgano tin ions. Examples of other biocides effective as antifouling agents are dithiocarbamate derivatives such as cuprous ethylene bis(dithiocarbamate) or 2-(N,N-dimethyl thiocarbamyl thio)-5-nitro thiazole, substituted isothiazolones particularly halogenated N-substituted isothiazolones, tetramethyl thiuram disulphide and dichlorodiphenyltrichloroethane (which also acts as a hydrophobic organic retarder).

The invention is illustrated by the following Examples:—

Example 1

Preparation of 8-quinolinyl acrylate

8-Hydroxyquinoline (58.0 g; 0.40 mole) was dissolved in a mixture of toluene (500 ml) and triethylamine (41.4 g; 0.41 mole). Acrylyl chloride (38.0 g; 0.42 mole) was added slowly, while

stirring, the reaction temperature being kept under 30°C. When the addition was complete the mixture was stirred for another 1 hour. The solution was then filtered and washed with a solution of sodium hydrogen carbonate in water followed by water only, and finally the toluene layer was dried with anhydrous sodium sulphate. Some toluene was evaporated off using a rotary evaporator under low pressure. The solution was left in a refrigerator overnight and the solid formed was filtered off. This was identified by infra-red and N.M.R. spectroscopy and micro-analysis to be 8-quinolinyl acrylate. Yield 48.6 g (61 per cent of the theoretical yield).

It was recrystallised from toluene to give crystals with m.p.:50—52°C.

Copolymerisation

8-Quinolinyl acrylate (12.3 g; 0.054 mole) was dissolved in cyclohexanone (63 g). Butyl acrylate (28.7 g; 0.224 mole) was added, followed by azobisisobutyronitrile (1.0 g). The solution was heated to 75°C and the polymerisation reaction was conducted with stirring at this temperature. A mild exotherm was observed in the first 15 minutes of the reaction. The course of the polymerisation was followed by observing the change in the refractive index. No further change was observed after 5 hours and the solution was heated to 100°C for a period of 30 minutes to destroy any residual activity of the azobisisobutyronitrile. The product was a solution of a 30:70 by weight copolymer of 8-quinolinyl acrylate and butyl acrylate.

Paint preparation

64.3 g of the quinolinyl acrylate butyl acrylate copolymer solution was diluted with 20.3 g cyclohexanone to give 84.6 g of a 29.5 per cent by weight solution. This was mixed with zinc oxide (67.5 g) and Aerosil colloidal silica (1.3 g) and milled overnight.

The paint obtained had a pigment volume concentration of 35 per cent and a solids content of 37 per cent by volume.

Example 2

Copolymerisation

8-Quinolinyl acrylate prepared as described in Example 1 (16.4 g; 0.072 mole) was dissolved in cyclohexanone (63 g). Butyl acrylate (24.6 g; 0.192 mole) was added, followed by azobisisobutyronitrile (1.0 g). The solution was heated to 75°C and the polymerisation reaction was conducted as described in Example 1. The product was a solution of a 40:60 by weight copolymer of 8-quinolinyl acrylate and butyl acrylate.

Paint preparation

66.7 g of the quinolinyl acrylate butyl acrylate copolymer solution was diluted with 18.7 g cyclohexanone to give 85.4 g of a 30.1 per cent by weight solution. This was mixed with zinc oxide

(67.5 g) and Aerosil colloidal silica (1.3 g) and milled overnight.

The paint obtained had a pigment volume concentration of 35 per cent and a solids content of 37 per cent by volume.

The smoothing performance of paints in relatively moving sea-water can be tested in the apparatus described in British patent specification 1,457,590 with reference to Figures 7A and 7B. A mild steel disc 31 having a diameter of 23 cm is coated overall with a conventional anti-corrosive paint and overcoated in radial stripes with the paints under test. The stripes are applied by a standardised applicator adapted to deposit a film 20 μ m thick (wet thickness).

The disc is immersed in flowing sea-water and rotated at a peripheral speed of 33 knots.

During this test the paint films under test are planed away, eventually to the extent that the underlying substrate (the anti-corrosive paint) is revealed. There is always some variation in the thickness of the paint film within each stripe so that the stripe of paint does not suddenly vanish; an increasing proportion of the substrate is revealed over time. When the substrate is revealed over 50 per cent of the area of the stripe it is a good approximation to say that the paint film in the stripe has lost by planing the original average dry thickness of the paint film in the stripe. The time in days to achieve this ("D⁵⁰") is a measure of the rate of planing of the paint in relatively moving sea-water.

The surface of the paint film in each stripe should be examined during the test to note whether it is smooth and firm. Paint films according to the invention which at least retain their initial smoothness must be distinguished from paint films which are removed over at least a portion of the stripe by flaking or localised erosion causing roughening or by separation from the disc.

The above test can be used to give an absolute rate of planing of the paint film, but the temperature, composition and flow rate of the sea-water can affect the result. The test is preferably used as a comparison in which one of the stripes painted on the disc is an anti-fouling paint known to have the desired rate of dissolution in relatively moving sea-water. The paint described in Example 1 of British patent specification 1,457,590, using copolymer C and 30 per cent by weight dichlorodiphenyl trichloroethane based on the organo tin content of the copolymer, is a paint which has been found to be successful in use on ships in service and can be used as a reference stripe in tests.

A disc was prepared having 2 stripes each of the paints of Examples 1 and 2, and 2 stripes of the above described paint of Example 1 of British patent specification 1,457,590.

All the paints were observed to be planed away during rotation in sea-water. The stripes of paint according to Example 1 of British patent specification 1,457,590 both had a D⁵⁰ of 12 days. The stripes of the paint of Example 1 of the present

application had a D⁵⁰ of 15 and 16 days and the stripes of the paint of Example 2 both had a D⁵⁰ of 16 days. These results indicate a rate of dissolution in relatively moving sea-water which would be sufficient to give appreciable smoothing of the paint film without its being dissolved away too fast and compatible with the release of sufficient of an added biocide without forming a leached inactive outer layer of paint.

Example 3

48.9 g of the copolymer solution prepared in the copolymerisation stage of Example 1 was mixed with 20.9 g zinc oxide, 22.2 g cuprous oxide, 0.8 g Aerosil, 1.5 g bentonite, 0.5 g n-butanol and 8.0 g cyclohexanone and milled overnight to produce a paint of pigment volume concentration 35 per cent and solids content 38 per cent by volume.

The paints of Examples 1 and 3 were both applied to a test panel. The panels were fixed to the bilge keel of a ferry operating in the Mediterranean. The panels were examined after 14 months in service, including 2 months in which the ferry was laid up in the Mediterranean. Areas around the test panels which were not coated with antifouling paint showed very heavy weed and animal fouling.

The paint of Example 1 which contained no biocide apart from zinc oxide and the copolymer, showed no fouling by seaweed and no adherent algal slime, although there was some fouling by tube worms. (Tube worms are known to be susceptible to many marine biocides such as cuprous oxide, zinc ethylene bis(dithiocarbamate) or triphenyl tin fluoride and a small amount of one of these could be added to the paint to boost its resistance to animal fouling). The paint of Example 1 was smoothed away from the panel at 5 μ m per month which is about the ideal rate to obtain a decrease in roughness of the paint film without using up the paint too fast; the commercially successful self-polishing organo tin copolymer paint used on the hull of the ship was smoothed away at 6 microns per month.

The paint of Example 3 shows no weed or animal fouling and only a little algal slime. This paint was smoothed away at 1 to 2 μ m per month; this may be rather slow to obtain any significant decrease in roughness.

Example 4

8-quinolinyl acrylate (12.3 g) and methyl methacrylate (28.7 g) were copolymerised under the conditions described in Example 1 to prepare a 39 per cent by weight solution of a 30:70 by weight copolymer of 8-quinolinyl acrylate and methyl methacrylate. 48.9 g of the copolymer solution was milled with 41.1 g zinc oxide, 0.8 g Aerosil, 1.5 g bentonite, 0.5 g n-butanol and 8.0 g cyclohexanone to produce a paint of pigment volume concentration 35 per cent and solids content 38 per cent by volume.

Example 5

14.35 g 8-quinolinyl methacrylate and 26.65 g

methyl methacrylate were copolymerised under the conditions described in Example 1 to prepare a 39 per cent by weight solution of a 35:65 by weight copolymer of 8-quinolinyl methacrylate and methyl methacrylate. A paint was prepared using the formulation of Example 4 except that 18 per cent of the copolymer was replaced with an equal volume of tritolyl phosphate plasticiser.

Example 6

18.45 g 8-quinolinyl methacrylate was copolymerised with 22.55 g methyl methacrylate using the conditions described in Example 1 to produce a 39 per cent by weight solution of a 45:55 by weight copolymer of 8-quinolinyl methacrylate and methyl methacrylate. A paint was prepared from the copolymer solution using the procedure of Example 5, including the plasticising by tritolyl phosphate.

Example 7

24.6 g 7-bromo-5-chloro-quinolinyl-8 acrylate was copolymerised with 16.4 g methyl methacrylate using the conditions of Example 1 to produce a 39 per cent by weight solution of a 60:40 by weight copolymer of 7-bromo-5-chloro-quinolinyl-8 acrylate and methyl methacrylate. A paint was prepared from the copolymer solution using the procedure of Example 4.

The smoothing performance of the paints of Examples 4 to 7 was tested using the test apparatus described in British patent specification 1,457,590 with reference to Figures 7A and 7B. The paints of Examples 4 to 7 were tested by comparison with a commercially successful organo tin copolymer paint. The results obtained were as follows:—

| | Average D ⁵⁰ (individual readings) |
|---------------------------------|---|
| Paint of Example 4 | 35 days (31, 39) |
| Paint of Example 5 | 20 days (only one stripe applied) |
| Paint of Example 6 | 14 days (only one stripe applied) |
| Paint of Example 7 | 13.5 days (14, 13) |
| Commerical paint for comparison | 18 days (16, 18, 20, 17, 17) |

The paints of Examples 4 to 7 all had a rate of dissolution similar to that of the commercial paint which has been successfully used in service, indicating that these paints would give appreciable smoothing of the paint film in service without its being dissolved away too fast.

All registered trade marks as noted in the above are acknowledged as such.

Claims

1. A marine paint comprising a film-forming copolymer and a metalliferous pigment which is sparingly soluble in sea-water, characterised in that the film-forming copolymer contains 20 to 80 per cent by weight of units of a quinolinyl or substituted quinolinyl ester of an olefinically unsaturated carboxylic acid, the balance of the copolymer being units of at least one olefinically unsaturated comonomer.

2. A marine paint according to claim 1, characterised in that the copolymer comprises 20 to 60 per cent by weight of the quinolinyl or substituted quinolinyl ester units.

3. A marine paint comprising a film-forming copolymer comprising units of a triorgano tin salt of an olefinically unsaturated carboxylic acid and units of at least one olefinically unsaturated comonomer, and a metalliferous pigment which is sparingly soluble in sea-water, characterised in that the copolymer comprises 10 to 80 per cent by weight of (a) units of a quinolinyl or substituted

quinolinyl ester of an olefinically unsaturated carboxylic acid, up to 60 per cent by weight of (b) units of a triorgano tin salt of an olefinically unsaturated carboxylic acid, (a) and (b) together forming 20 to 80 per cent by weight of the copolymer, and the balance of the copolymer is units of at least one olefinically unsaturated comonomer.

4. A marine paint according to claim 3, characterised in that the copolymer comprises from 15 to 40 per cent by weight of (a), from 20 to 45 per cent by weight of (b) and from 30 to 50 per cent by weight of units of at least one alkyl acrylate or methacrylate.

5. A marine paint according to any of claims 1 to 4, characterised in that the quinolinyl or substituted quinolinyl ester units are 8-quinolinyl acrylate units.

6. A marine paint according to any of claims 1 to 4, characterised in that the quinolinyl or substituted quinolinyl ester units are 8-quinolinyl methacrylate units.

7. A marine paint according to any of claims 1 to 6, characterised in that units of an alkyl acrylate or methacrylate ester constitute the balance of the film-forming copolymer.

8. A marine paint according to any of claims 1 to 7, characterised in that the metalliferous pigment is a mixture of zinc oxide with cuprous oxide, cuprous thiocyanate or zinc ethylene bis(dithiocarbamate).

9. A marine paint according to claim 8, charac-

terised in that the metalliferous pigment is a mixture of zinc oxide with cuprous oxide or cuprous thiocyanate in a ratio of 1:1 to 9:1 by weight.

10. A ship, characterised in that at least part of its sub-marine surface has been painted with a marine paint according to any of claims 1 to 9.

Patantansprüche

1. Unterwasserfarbe mit einem Gehalt an einem filmbildenden Copolymer und einem in Seewasser schwerlöslichen metallhaltigen Pigment, dadurch gekennzeichnet, dass das filmbildende Copolymer 20—80 Gew.-% Einheiten eines ggf. substituierten Chinolinylesters einer olefinisch ungesättigten Carbonsäure enthält, wobei die restlichen auf das Copolymer bezogenen Einheiten wenigstens ein olefinisch ungesättigtes Comonomer darstellen.

2. Unterwasserfarbe nach Anspruch 1, dadurch gekennzeichnet, dass das Copolymer 20—60 Gew.-% Einheiten eines ggf. substituierten Chinolinylester enthält.

3. Unterwasserfarbe mit einem Gehalt an einem filmbildenden Copolymer mit Einheiten eines Triorganozinnsalzes einer olefinisch ungesättigten Carbonsäure und Einheiten wenigstens eines olefinisch ungesättigten Comonomers sowie einem in Seewasser schwerlöslichen metallhaltigen Pigment, dadurch gekennzeichnet, dass das Copolymer jeweils Einheiten von (a) 10—80 Gew.-% eines ggf. substituierten Chinolinylesters einer olefinisch ungesättigten Carbonsäure und (b) bis zu 60 Gew.-% eines Triorganozinnsalzes einer olefinisch ungesättigten Carbonsäure enthält, wobei (a) und (b) zusammen 20—80 Gew.-% des Copolymers ausmachen und die restlichen auf das Copolymer bezogenen Einheiten wenigstens ein olefinisch ungesättigtes Comonomer darstellen.

4. Unterwasserfarbe nach Anspruch 3, dadurch gekennzeichnet, dass das Copolymer jeweils Einheiten von 15—40 Gew.-% von (a), 20—45 Gew.-% von (b) und 30—50 Gew.-% wenigstens eines Alkylacrylates oder -methacrylates enthält.

5. Unterwasserfarbe nach einem der Ansprüche 1—4, dadurch gekennzeichnet, dass die Einheiten des ggf. substituierten Chinolinylesters in Form von 8-Chinolinylacrylat vorliegen.

6. Unterwasserfarbe nach einem der Ansprüche 1—4, dadurch gekennzeichnet, dass die Einheiten des ggf. substituierten Chinolinylesters in Form von 8-Chinolinylmethacrylat vorliegen.

7. Unterwasserfarbe nach einem der Ansprüche 1—6, dadurch gekennzeichnet, dass die Einheiten des Alkylacrylat oder -methacrylatesters den restlichen Anteil des filmbildenden Copolymers darstellen.

8. Unterwasserfarbe nach einem der Ansprüche 1—7, dadurch gekennzeichnet, dass das metallhaltige Pigment eine Mischung aus Zinkoxyd und Kupferoxyd oder Kupferthiocyanat bzw. Zinkäthylbis-(dithiocarbamat) darstellt.

9. Unterwasserfarbe nach Anspruch 8, dadurch

gekennzeichnet, dass metallhaltige Pigment eine Mischung aus Zinkoxyd und Kupferoxyd der Kupferthiocyanat im Gewichtsverhältnis von 1:1 bis 9:1 darstellt.

10. Schiff, dadurch gekennzeichnet, dass wenigstens ein Teil seiner unter Wasser befindlichen Oberfläche mit einer Unterwasserfarbe nach einem der Ansprüche 1—9 gestrichen worden ist.

Revendications

1. Peinture marine comprenant un copolymère filmogène et un pigment métallifère difficilement soluble dans l'eau de mer, caractérisé en ce que le copolymère filmogène contient 20 à 80 pour cent en poids de motifs d'un ester quinoléique ou quinoléique substitué d'un acide carboxylique à insaturations oléfiniques, le reste du copolymère étant constitué de motifs d'au moins un comonomère à insaturations oléfiniques.

2. Peinture marine selon la revendication 1, caractérisée en ce que le copolymère comprend 20 à 60 pour cent en poids de motifs ester quinoléique ou quinoléique substitué.

3. Peinture marine comprenant un copolymère filmogène contenant des motifs d'un sel triorgano-étain d'un acide carboxylique à insaturations oléfiniques et des motifs d'au moins un comonomère à insaturations oléfiniques et un pigment métallifère difficilement soluble dans l'eau de mer, caractérisée en ce que le copolymère comprend 10 à 80 pour cent en poids de (a) motifs d'un ester quinoléique ou quinoléique substitué, jusqu'à 60 pour cent en poids de (b) motifs d'un sel triorgano-étain d'un acide carboxylique à insaturation oléfiniques, (a) et (b) ensemble formant 20 à 80 pour cent en poids du copolymère et le reste du copolymère étant constitué de motifs d'au moins un comonomère à insaturations oléfiniques.

4. Peinture marine selon la revendication 3, caractérisée en ce que le copolymère comprend de 15 à 40 pour cent en poids de (a), de 20 à 45 pour cent en poids de (b) et de 30 à 50 pour cent en poids de motifs d'au moins un acrylate ou méthacrylate d'alkyle.

5. Peinture marine selon l'une quelconque des revendications 1 à 4, caractérisée en ce que les motifs d'ester quinoléique ou quinoléique substitué sont des motifs d'acrylate 8-quinoléique.

6. Peinture marine selon l'une quelconque des revendications 1 à 4, caractérisée en ce que les motifs d'ester quinoléique ou quinoléique substitué sont des motifs de méthacrylate 8-quinoléique.

7. Peinture marine selon l'une quelconque des revendications 1 à 6, caractérisée en ce que les motifs d'un ester acrylate ou méthacrylate constituent le reste du copolymère filmogène.

8. Peinture marine selon l'une quelconque des revendications 1 à 7, caractérisée en ce que le pigment métallifère est un mélange d'oxyde de zinc et d'oxyde cuivreux, de thiocyanate cuivreux ou d'éthylène-bis(dithiocarbamate) de zinc.

9. Peinture marine selon la revendication 8, caractérisée en ce que le pigment métallifère est un mélange d'oxyde de zinc et d'oxyde cuivreux ou de thiocyanate cuivreux, en proportion pondérale de 1:1 à 9:1.

10. Bateau, caractérisé en ce qu'au moins une partie de sa surface submergée a été peinte avec une peinture marine selon l'une quelconque des revendications 1 à 9.

5

10

15

20

25

30

35

40

45

50

55

60

65

8